

## HETEROGENEOUS PHOTOCATALYSIS OF IMIDACLOPRID THE EFFECT OF REACTION PARAMETERS

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### Abstract

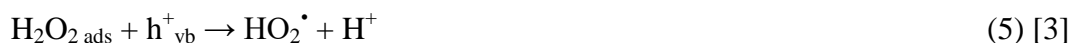
The heterogeneous photocatalytic transformation of a harmful neonicotinoide insecticide, imidacloprid using TiO<sub>2</sub> photocatalyst was the aim of the present work. The optimal TiO<sub>2</sub> concentrations in oxygenated, aerated and oxygen-free suspensions were determined. However the dissolved oxygen enhanced the transformation rate of imidacloprid that was occurred in oxygen-free suspensions too. This can be explained by the relative high reactivity of imidacloprid towards hydrated electron, thus the relative contribution of direct charge can be significant. The effect of different additives was investigated to prove this assumption: NaF, methanol, *t*-butanol, chloroform, EDTA and KI. The pH and ionic strength of the solution have also significant effect, most likely by modifying the surface properties of TiO<sub>2</sub>. The results showed, that beside HO• based reaction the direct charge transfer must have significant role in the transformation of imidaclopride.

### Introduction

Imidacloprid is an insecticide belonging to the neonicotinoids, a class of chemicals which attack the nervous system of insects. It is a widely used insecticide in agriculture, although - along three other neonicotinoids - the European Union banned its use in 2018, due to its harmful effects on beneficial insects, like honeybees. [1]

Heterogeneous photocatalysis is a possible supplementary water treatment method for the removal of imidacloprid from waters. During the irradiation of the photocatalyst with light having higher energy than the band gap of the catalyst, the separation of charges creates an electron ( $e_{cb}^-$ ), and a positively charged hole ( $h_{vb}^+$ ). To avoid the recombination of charges, the  $e_{cb}^-$  must be trapped using an effective electron scavenger, usually dissolved oxygen takes this role. The most reactive species during heterogeneous photocatalysis are the hydroxyl radicals (HO•). They may form via their reaction of the  $h_{vb}^+$  with water or HO<sup>-</sup> (1-2), or due to the reaction of  $e_{cb}^-$  with oxygen, resulting in O<sub>2</sub>•<sup>-</sup>. The further transformation of O<sub>2</sub>•<sup>-</sup> produces H<sub>2</sub>O<sub>2</sub>, and finally HO• (3-5) [2]. During the heterogeneous photocatalysis of imidacloprid, it is reported, that HO• has an important role. [4]





The goal of our work was to determine the dissolved oxygen and  $\text{TiO}_2$  concentration dependency of the photocatalytic process efficiency. Moreover the effect of various additives was determined to get information about the relative contribution of the  $\text{HO}^\bullet$  and direct charge transfer based reactions to the transformation of imidacloprid. We used ionic compounds, such as  $\text{NaCl}$  ( $\text{Cl}^-$  has no special affinity to the  $\text{TiO}_2$  surface) and  $\text{NaF}$  ( $\text{F}^-$  can replace  $-\text{OH}$  of  $\text{TiO}_2$  surface and consequently change the surface properties, such as adsorption capacity). Methanol and *t*-butanol were applied as  $\text{HO}^\bullet$  scavengers, while chloroform was used as  $\text{O}_2^{\bullet-}$  scavenger.  $\text{KI}$  ( $\text{I}^-$ ) and  $\text{EDTA}$  are able to decrease significantly the contribution of both direct charge transfer (through the reaction with  $h^+_{\text{vb}}$ ) and  $\text{HO}^\bullet$  based reactions via competition with imidacloprid for these reactive species. Additives were applied in 1:1, 10:1, 50:1 molar ratios to the imidacloprid. We also investigated the effect of pH (3.0, 6.5, 9.0).

### Experimental

Aqueous solutions of imidacloprid ( $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) were irradiated using a fluorescent UV light source (300-400nm).  $\text{TiO}_2$  (Degussa P25 Aeroxide) were used in different concentrations ( $0\text{--}1.5 \text{ g dm}^{-3}$ ), the suspension was sonicated before the irradiation. During the measurement, the suspension was stirred and circulated in a thermostated glass reactor. The suspension was saturated with oxygen, air or nitrogen.  $\text{NaCl}$ ,  $\text{NaF}$ , methanol, *t*-butanol, chloroform,  $\text{KI}$ , and  $\text{EDTA}$  were added in  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $1.0 \times 10^{-3} \text{ mol dm}^{-3}$  and  $5.0 \times 10^{-3} \text{ mol dm}^{-3}$  concentrations (1:1, 10:1, 50:1 molar ratios to the imidaclopride). The pH was adjusted with  $\text{HCl}$  and  $\text{NaOH}$ .

The samples were centrifuged and filtered before analysis using  $0.22 \mu\text{m}$  syringe filters. The degradation rate of imidacloprid was determined using an Agilent 1100 series HPLC equipped with a LiChrospher® 100 RP-18 column and a diode array detector ( $\lambda=270 \text{ nm}$ ). The eluent was a mixture of methanol and water (40:60 ratio).

### Results and discussion

Imidacloprid does not adsorb significantly on the  $\text{TiO}_2$  surface: using  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  imidacloprid addition of  $1.0 \text{ g dm}^{-3}$   $\text{TiO}_2$  had no effect on the imidacloprid concentration in the aqueous phase. The optimal  $\text{TiO}_2$  concentration in suspensions bubbled through with oxygen, nitrogen (oxygen-free suspension) and air were also determined.

Without  $\text{TiO}_2$  there is a slow transformation of imidacloprid due to the small overlap of the spectrum of imidacloprid and the emitted light of the lamp. Dissolved oxygen concentration has no effect in these cases, when the transformation of imidacloprid takes place via direct photolysis. Increasing the  $\text{TiO}_2$  dosage the competitive light absorption between imidacloprid and  $\text{TiO}_2$  particles became more important, and direct photolysis is fully suppressed by the absorption of photons by  $\text{TiO}_2$  particles above  $0.50 \text{ g dm}^{-3}$ . In oxygen containing suspensions the transformation rate increased with  $\text{TiO}_2$  dosage and there was not found significant difference in the transformation rates using air or oxygen. The optimal dosage of  $\text{TiO}_2$  was about  $0.50 \text{ g dm}^{-3}$ .

In oxygen-free suspensions the optimal  $\text{TiO}_2$  dosage was lower, between  $0.25$  and  $0.50 \text{ g dm}^{-3}$  and the dose dependence of the transformation rate was found to be different than in oxygen-containing ones. Effective transformation via heterogeneous photocatalytic way requires the presence of effective  $e^-_{\text{cb}}$  scavenger, which is generally dissolved oxygen. In most cases there is no transformation of organic substances in oxygen-free suspensions. However in the case of heterogeneous photocatalysis of imidacloprid the transformation rate showed maximum between  $0.25$  and  $0.50 \text{ g dm}^{-3}$ , and reached a plateau above  $0.75 \text{ g dm}^{-3}$   $\text{TiO}_2$  dosage. The

value of the transformation rate above this photocatalyst dosage is less than the half of that determined in oxygen containing suspension. At lower  $\text{TiO}_2$  dosage the transformation takes place by direct photolysis and heterogeneous photocatalysis. The relative contribution is depend on the  $\text{TiO}_2$  dosage. The increase in the  $\text{TiO}_2$  dosage reduces the importance of direct photolysis, and the overall effectiveness decreases. The efficiency of heterogeneous photocatalysis without oxygen can be explained by the relative high reactivity of imidacloprid toward  $e_{\text{aq}}^-$ . Thus imidacloprid is able behaves as  $e_{\text{cb}}^-$  scavenger instead of dissolved oxygen. In this case the transformation must take place mainly by direct charge transfer.

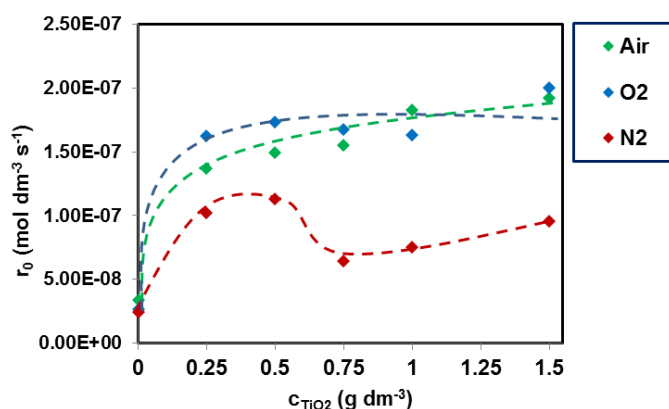


Figure 1. Transformation rates of imidacloprid using different concentrations of  $\text{TiO}_2$  and dissolved oxygen

For further experiments we used  $1.0 \text{ g dm}^{-3}$   $\text{TiO}_2$  concentration to avoid direct photolysis and suspensions were bubbled with oxygen to optimize the formation rate of  $\text{HO}\cdot$ . The role of direct charge transfer and  $\text{HO}\cdot$  based reactions were investigated via effect of various additives. Inorganic ions affect the photocatalytic process by increasing ionic strength, changing the surface charge and the adsorption properties of target compounds on  $\text{TiO}_2$  particles. We used  $\text{NaCl}$  to investigate the effect of ionic strength increase, since  $\text{Cl}^-$  has no any kind of specific interaction with  $\text{TiO}_2$  surface. Addition of  $\text{NaCl}$  has no significant effect on degradation rate.

$\text{F}^-$  has a special affinity for the  $\text{TiO}_2$  surface, replacing surface  $-\text{OH}$  groups with  $-\text{F}$  groups. Addition of  $\text{NaF}$  affects the efficiency of photocatalytic transformation in many cases by various ways. It is accepted, that  $\text{F}^-$  increases the  $\text{HO}\cdot$  concentrations in the bulk solution by improved electron transfer capabilities, decreasing charge recombination, and increasing the possibility of  $h_{\text{vb}}^+$  based reactions. [5]  $\text{NaF}$  addition to the imidacloprid solution did not change its adsorption, but slightly increased the degradation rates when compared to the effect of  $\text{NaCl}$ , indicating the importance of  $\text{HO}\cdot$  during the transformation process. It was also confirmed by the results of methanol and *t*-butanol addition. Both alcohol is effective  $\text{HO}\cdot$  scavenger and significantly decreased the transformation rate of imidacloprid when used in higher concentrations.

Dissolved oxygen reacts with the photogenerated  $e_{\text{cb}}^-$ , forming  $\text{O}_2^{\cdot-}$ , which may also react with certain compounds. Chloroform was used, as a  $\text{O}_2^{\cdot-}$  scavenger to investigate its possible effect. Chloroform did not hinder the transformation of imidacloprid, proving the negligible effect of  $\text{O}_2^{\cdot-}$ .

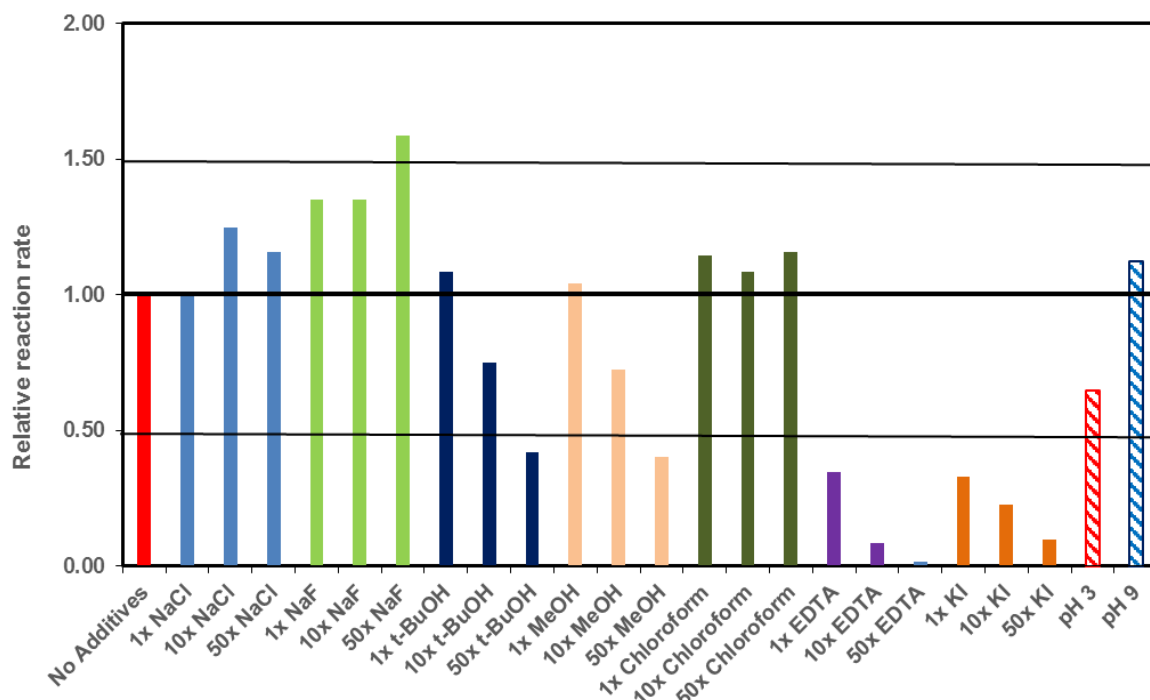


Figure 2. Relative transformation rates of imidacloprid in the case of different additives, compared to the reaction rate when no additives were used

Imidacloprid transformation is assumed partly by direct charge transfer reactions. To prove this assumption, the effect of EDTA and KI as a scavenger of  $h_{\nu b}^+$  was determined. EDTA adsorbs well on the  $TiO_2$  surface, where it can easily react with  $h_{\nu b}^+$ , hindering not only the transformation of other compound via direct charge transfer, but also the formation of  $HO\bullet$  and other hole-induced reactions. Addition of EDTA even at 1:1 molar ratios had a more significant effect than alcohols at 50:1 ratios. At higher concentrations, EDTA nearly completely inhibits the transformation of imidacloprid (10:1 and 50:1 ratio). Similar effect of  $I^-$  (KI), which is a well-known scavenger of both  $h_{\nu b}^+$  and  $HO\bullet$  was experienced. Its effect is slightly less pronounced at higher dosages than EDTA, most likely because of its less significant adsorption. These results prove both the importance of surface accessibility during the photocatalytic degradation of imidacloprid, and the possibility of the direct charge transfer despite the negligible adsorption of imidacloprid on the  $TiO_2$  surface.

We also investigated the effect of the pH, performing experiments on pH 6.5, on the estimated point of zero charge (PZC) of  $TiO_2$ , on pH 3.0 and pH 9.0. Changing the pH has several complex effects: changes the surface charge of  $TiO_2$  from neutral to positive (acidic conditions) or to negative (basic conditions). This may influence the adsorption on the  $TiO_2$  surface, and other surface properties, and also the formation of reactive species. We found that on pH 3.0 the transformation rate of imidacloprid significantly lowered, while on pH 9.0 it slightly increased.

## Conclusion

- The transformation rate of a harmful pesticide, imidacloprid using heterogeneous photocatalysis was investigated.
- The  $TiO_2$  dosage was optimized under oxygen saturated and oxygen free conditions.
- Effect of  $HO\bullet$  radical scavengers (methanol, *t*-butanol, chloroform) proved the significant role of  $HO\bullet$  in the transformation of imidacloprid.

- The effect of EDTA and KI proved the importance of direct charge transfer beside HO• based reaction in the transformation of imidacloprid

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